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(54) LEAD-FREE SOLDER AND PACKAGING METHOD USING THE SAME AND PACKAGED ARTICLES

(57)Abstract:
PROBLEM TO BE SOLVED: To make it possible to execute lead-free soldering within the heat resistant temp. of a glass epoxy substrate by using lead-free solder specified in the contents of Zn, Bi and Sn.
SOLUTION: The lead-free solder is composed, by mass %, of <4 to 5% Zn, 13 to 16% Bi and the balance Sn. The org. insulating substrate is printed with such Zn-Bi-Sn solder paste and the solder paste is melted at the heat resistant temp. of the org. insulating substrate or below, by which the org. insulating substrate and its mounting parts are connected. The glass epoxy substrate, etc., are used for the org. insulating substrate and electronic parts are packaged thereon. This lead-free solder is used for BGA packages or as balls, etc., for chip carriers. The lead-free solder ensures reflow at about ≤220° C. The reflow at ≥150° C is warranted. The reflow by assuring the sufficient wettability on Cu conductors with a weak flux or with the Sn solder plated terminal constitution of parts is made possible. This solder is substitutive for Sn-Pb eutectic solder.

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[Claim(s)]
[Claim 1] Lead-free soldering characterized by having made less than [more than 4mass%5mass%] and Bi less than more than 13mass%16mass%, and setting the remainder to Sn for Zn in the solder which consists of Zn-Bi-Sn.
[Claim 2] In the substrate mounting method using the solder of the lead freelancer who consists of Zn-Bi-Sn [the soldering paste which consists Zn of Zn-Bi-Sn which made less than more than 4mass%6mass% and Bi less than more than 13mass%16mass%, and set the remainder to Sn / printing to an organic insulated substrate] The substrate mounting method using the lead-free soldering characterized by melting said soldering paste below at a heat-resistant temperature of said organic insulated substrate, and connecting said organic insulated substrate and its loading component.
[Claim 3] In the substrate mounting method using the solder of the lead freelancer who consists of Zn-Bi-Sn For Zn less than more than 4mass%6mass% and Bi Less than more than 13mass% 16mass% The substrate mounting method using the lead-free soldering characterized by melting below at a heat-resistant temperature of said organic insulated substrate using the solder which consists of Zn-Bi-Sn which set the remainder to Sn, and connecting said organic insulated substrate and its loading component.
[Claim 4] Zn for an organic insulated substrate, the loading components carried in said organic insulated substrate, and said organic insulated substrates and said loading components Less than more than 4mass%6mass% The mounting article by the lead-free soldering bonding characterized by connecting with the solder which consists of Zn-Bi-Sn which made Bi less than more than 13mass% 16mass%, and set the remainder to Sn.

[Claim 5] weight (mass) % labeling of a presentation [in / on soldering of an organic insulated substrate, and / Zn-Bi-Sn3 element system] -- coordinates (Zn --) Lead-free soldering for organic insulated substrate bonding characterized by using the alloy solder of the presentation which displays by Bi and Sn, is surrounded by A (6, 16, **), B (6, 13, **), C (5.5, 12, **), D (4.5, 14, **), and E (3.7, 16, **), and changes.
[Claim 6] The substrate mounting method and mounting article using the lead-free soldering and lead-free soldering which are characterized by said organic insulated substrate being a glass epoxy board in Claim 2 or Claim 5.
[Claim 7] The substrate mounting method and mounting article using the lead-free soldering and lead-free soldering which are characterized by using Ag, Cu, Sb, In, or its combination as the additive of said lead-free soldering further in Claim 1 or Claim 6.
[Claim 8] The substrate mounting method and mounting article using the lead-free soldering and lead-free soldering which are characterized by using said lead-free soldering as a ball for the object for a BGA (Ball Grid Array) package, or chip carriers in Claim 1 or Claim 7.
[Claim 9] In Claim 1 or Claim 8, a terminal is supplied for said lead-free soldering with a wire bond. The substrate mounting method and mounting article using the lead-free soldering and lead-free soldering which are characterized by filling up between a chip and a substrate with resin (500 to 1000 kgf/mm2 Young's modulus, and coefficient-of-thermal-expansion 15x10~6-/degree C - 35x10~6-/degree C).

[Detailed Description of the Invention]
[0001]
[Industrial Application] In order that this invention may connect LSI, components, etc. to a glass epoxy board. Soldering in the maximum temperature of 220 degrees C is possible, and it is related with the mounting article using the soldered-joint method and it using the Sn-Zn-Bi system lead-free soldering and it which guarantee the bonding reliability under the elevated temperature in 150 degrees C.
[0002]
[Description of the Prior Art] The printed plate board construction material currently generally used is a product made from glass epoxy. A heat-resistant temperature of a glass epoxy board is usually 220 degrees C, when a reflow furnace is used. As a presentation of the solder for bonding used for this, the thing Sn-37mass%Pb eutectic solder (fusing point: 183 degrees C) or near the eutectic was common. from it being around 183 degrees C, these fusing points can make bonding sufficient at below a heat-resistant temperature (220 degrees C) of the glass epoxy board currently used widely, and guarantee a maximum of 150 degrees C of the reliability -- things were able to be carried out.
[0003] If it is neglected to carry out ** common, and the lead (it is hereafter described as Pb) contained in this solder reacts easily with an acid, and melts into ground water (acid rain is also

accelerated) and the printed plate board currently used for electronic parts in the U.S. is used for potable water these days, having an adverse effect on a human body is announced officially, and it has been a problem. Then, as a Pb free solder replaced with Sn-Pb system solder, there is little effect on environment, there is little toxicity to a human body, there are few problems of depletion of a resource, there are also few problems in respect of cost, and a close-up of Sn, Zn, Bi, etc. with the operating experience as an ingredient etc. is taken as a major candidate. With 2 element-system solder, Sn-3.5mass%Ag (221 degrees C of fusing points) and Sn-5mass%Sb (240 degrees C of fusing points) already have an operating experience as Pb free solder.

[0004] However, since these solder has the too high fusing point compared with Sn-Pb eutectic solder, it cannot secure bonding sufficient at below a heat-resistant temperature (220 degrees C) of a glass epoxy board, and cannot use it for the soldering.

[0005] Although there is Sn-9mass%Zn (eutectic of 199 degrees C of fusing points) as other solder ingredients, it is not such a low fusing point that this can also carry out a reflow of the electronic parts at 220 degrees C which is a heat-resistant temperature of a glass epoxy board. Moreover, even if it uses flux (chlorine 0.2mass% inclusion) of a rosin system currently generally used, in the reflow temperature of 220 degrees C, it turns out that it can hardly apply. Since the amount of this solder ingredient of Zn increases, the surface will oxidize easily remarkably and the wettability over Cu or nickel will fall remarkably compared with a Sn-Ag system and a Sn-Sb system.

[0006] On an old track record, although one high 30-50 degrees C is experientially known to the fusing point of solder as for soldering temperature, when wettability is bad, this temperature gradient becomes large further.

[0007] Although there are Sn-Bi system solder (representation presentation Sn-58mass%Bi; 138 degrees C of fusing points) and Sn-In system solder (representation presentation Sn-52mass%In; 117 degrees C of fusing points) other than these these cannot guarantee high temperature strength of 150 degrees C, when solidus temperature falls -- Sn-37mass% -- it cannot be said to be the solder for Pb eutectic solder alternative.

[0008] Moreover, although Sn-2%Ag-7.5%Bi-0.5% Cu (liquidus temperature: degrees C [211], solidus temperature:183 degree C) of 4 element-system Pb free solder ingredient is also proposed by the Sn-Ag system, since the fusing point is still high, a reflow within a heat-resistant temperature of a glass epoxy board is difficult too. Moreover, plural systems, therefore component control are difficult. Furthermore, in a thermal analysis, if the solidus of the low temperature of a 130-degree-C level is detected slightly and lowers liquidus temperature:211 degree C further, the solidus temperature of 130-degree C low temperature will appear clearly.

[0009] That is, except the Sn-Zn system, the solder ingredient in which a 220-degree-C reflow is possible is not found out without having a low-temperature solidus.

[0010] There are a Sn-Zn-In system and a Sn-Zn-Bi system in the solder ingredient which avoids this problem as a principal component. It decided to examine three element systems of a Sn-Zn-Bi system which is the combination of an element with an operating experience this time in

consideration of lowering of the lifetime by a reaction with cost, toxicity, corrosion resistance, and weatherproof flux etc. This solder is considered to be promising also from the field of a fusing point besides the above-mentioned evaluation criteria.

[0011] Drawing 1 is the well-known phase diagram [International Crit-ical Tables, 2 (1927), 418] of 3 element-system solder of Sn-Zn-Bi. Although the temperature distribution of the whole rough fusing point (liquidus temperature) is known, it is the actual condition which detailed distribution, a clear temperature, etc. do not understand. That is, the connection of the liquidus temperature and solidus temperature which are needed here is unknown. A dotted line is a 2 yuan eutectic line. Other continuous lines show the isothermal line of each temperature.

[0012] About Sn-Zn-Bi system solder, JP,S57-11793,A and JP,S59-189096,A have a description.

[0013] In JP,S57-11793,A, the solder for low-melt point point aluminum excellent in the corrosion resistance which 5 - 10mass% becomes in Zn, and the remainder becomes from Sn 8 - 13mass% in Bi is proposed. This is not aimed at bonding with the printed plate board which consists of a Cu conductor for the purpose of the improvement in hardness with the solder for aluminum. As a Reason for having decided this range of Zn (5 - 10mass%) and Bi (8 - 13 mass%), in the case of Zn, the lack of soldering hardness with aluminum is pointed out, and 7 - 9mass% is desirably shown by less than [;5mass%]. Moreover, if;13mass% is exceeded in Bi, **** of solder will be lost, and workability supposes that it is bad. That is, these conditions are the soldering hardness at the time of targetting aluminum, and viscosity, and are not taken into consideration about the printed plate board which consists of a Cu conductor. Moreover, although this presentation field is decided based on **** of a fusing point, hardness, and melting solder, only two samples being indicated, and that data not existing about **** of melting solder, and determining the presentation of Sn-Zn-Bi in the example of Sn-Zn-Bi3 element system, has many ambiguous portions.

[0014] On the other hand, as for JP,S59-189096,A, the solder which the remainder becomes [Zn] from Sn 3 - 20mass% 5 - 15mass% in Bi is proposed. This aims at the improvement in hardness in bonding of a wire, and is not taken as the object of bonding of the printed plate board which consists of a Cu conductor. As a Reason for deciding this range of Zn (5 - 15mass%) and Bi (3 - 20mass%), in the case of Zn, less than [;5mass%], when the point that hardness is insufficient, and the addition were increased, hardness increased, and melting temperature also rose, and it is indicated that the point which becomes weak exceeds 15mass%. In moreover, the case of Bi; it is carrying out to if 20mass% is exceeded and solder will become weak. Although this presentation field is decided based on a fusing point or bond strength, there is no set point of a fusing point and the analyses process of the fusing point using 3 element-system phase equilibrium phase diagram is not shown. Therefore, the presentation dependency of a fusing point is not clear too.

[0015]

[Problem to be solved by the invention] Since this invention mounts electronic parts, such as LSI and components, in the conventional glass epoxy board by high reliance using the solder for an alternative of Sn-Pb eutectic solder without including Pb, It aims at being able to carry out a reflow

below 220 degrees C, guaranteeing 150 degrees C or more, and securing wettability and fully being able to carry out a reflow of it in weak flux, with Sn system solder metal-plating terminal architecture of components on Cu conductor.

[0016] For this reason, at least 150 degrees C or more of solidus temperature of a fusing point is 160 degrees C or more (it can be equal to the 150-degree C activity in an elevated temperature) desirably. Liquidus temperature made the technical problem a maximum of 195 degrees C or less of things desirably considered as 190 degrees C or less (soldering temperature becomes high and the thermal effect to a substrate and components becomes large, as for making it high). Although some can be covered by the meta-rise on a terminal in wettability reservation, in order to prevent the badness of the wet by the physical properties of the ingredient itself, it is necessary to press down the amount of bad Zn of wet to the minimum. However, since liquidus temperature does not fall greatly unless it puts in Zn, it is necessary to maintain balance with wet and to decide a presentation. in Sn-Zn2 element system -- Sn -- Zn -- 9mass% -- although it becomes the minimum of a 199-degree C fusing point in the condition of having put in, in the reflow which a fusing point is high and is still 220 degrees C now, wet is too bad as mentioned above.

[0017] That is, the first object of this invention is to offer the presentation of the solder which can mount electronic parts, such as LSI and components, in organic insulated substrates, such as the conventional glass epoxy board, by high reliance in the solder which does not contain Pb, i.e., the solder which consists of Sn-Zn-Bi. A reflow can be carried out below 220 degrees C, and, specifically, it is flux weak [guaranteeing 150 degrees C or more]. It is in fully securing wettability with Sn system solder metal-plating terminal architecture of components on Cu conductor, and offering the solder which can carry out a reflow.

[0018] The second object of this invention is to mount electronic parts, such as LSI and components, in organic insulated substrates, such as a glass epoxy board, by high reliance using the solder which does not contain Pb.

[0019] The third object of this invention is to offer the mounting article mounted in organic insulated substrates, such as a glass epoxy board, using the solder which does not contain Pb.

[0020]

[Means for solving problem] In order to attain the above-mentioned object, there is little effect on environment in Pb free solder. There was little toxicity, it excelled in corrosion resistance and creep resistance, and fusing point temperature could be lowered, and the temperature gradient with liquidus temperature and solidus temperature was made small, the reliability at the time of bonding was raised, and the alloy which used as the base 3 element-system solder of Sn-Zn-Bi which can secure wettability further was examined as a candidate. As shown in drawing 1 until now, it is the grade which the outline of a fusing point (liquidus temperature) understands, and the detail of the phase diagram of this 3 element-system solder is strange. For this reason, it is necessary to clarify connection, such as connection between a fusing point (solidus temperature, liquidus temperature) and a presentation, a presentation and wettability, physical properties, and a mechanical property,

etc. Then, it started with making a Sn-Zn-Bi3 element-system phase diagram.

[0021] And in order to attain said first object, in the solder which consists of Zn-Bi-Sn, less than [more than 4mass%5mass%] and Bi were made less than more than 13mass%16mass%, and the remainder was set to Sn for Zn. Or weight (mass) % labeling of the presentation was expressed as coordinates (Zn, Bi, Sn), and it was considered as 3 element-system presentation of a Sn-Zn-Bi system of the presentation which is surrounded by A (6, 16, **), B (6, 13, **), C (5.5, 12, **), D (4.5, 14, **), and E (3.7, 16, **), and changes.

[0022] In the substrate mounting method using the solder of the lead freelancer who consists of Zn-Bi-Sn in order to attain said second object [the soldering paste which consists Zn of Zn-Bi-Sn which made less than more than 4mass%6mass% and Bi less than more than 13mass%16mass%, and set the remainder to Sn / printing to an organic insulated substrate] Said soldering paste was melted below at a heat-resistant temperature of said organic insulated substrate, and said organic insulated substrate and its loading component were connected.

[0023] The loading components carried in an organic insulated substrate and said organic insulated substrate in order to attain said third object, Said organic insulated substrate and said loading component were used as the mounting article connected with the solder which consists Zn of Zn-Bi-Sn which made less than more than 4mass%6mass% and Bi less than more than 13mass% 16mass%, and set the remainder to Sn.

[0024] Furthermore, wettability was secured by using the paste made and crowded with the process in which the solder surface does not oxidize for wettability reservation, and connecting by N2 reflow and a vapor reflow.

[0025]

[Function] In Zn, Bi 4 - 6mass% Thus, 13 - 16mass%, the remainder sets to Sn -- or weight (mass) % labeling of a presentation -- coordinates (Zn --) By considering it as 3 element-system presentation of a Sn-Zn-Bi system of the presentation which displays by Bi and Sn, is surrounded by A (6, 16, **), B (6, 13, **), C (5.5, 12, **), D (4.5, 14, **), and E (3.7, 16, **), and changes The characteristics which lowered liquidus temperature, and secured the mechanical reliability in the elevated temperature as solder for glass epoxy board bonding, and were excellent in reflow nature (a temperature gradient with liquidus temperature and solidus temperature is lessened) are acquired. And the wettability to Cu board is secured and a good mechanical property is reconciled.

[0026] The Reason which limited the solder presentation above is as follows.

[0027] To bonding, it is desirable to lessen a temperature gradient with liquidus temperature and solidus temperature as much as possible. Because, noises, such as an oscillation at the time of conveyance, can be considered according to the cooling process of a reflow. For this reason, if a temperature gradient with liquidus temperature and solidus temperature is large, since solid phase and the time at the time of liquid phase coexistence are long, the probability that noises, such as an oscillation, will enter will become high. For this reason, it is easy to produce a bonding defect and there is a possibility that a problem may appear in the reliability of a joint. The temperature gradient of

liquidus temperature and solidus temperature has large Zn at less than 4mass%, and bonding at 220 degrees C or less is difficult. The above-mentioned temperature gradient becomes large more than 6mass%. Moreover, according to the tension test by Sn-xZn-15Bi (the amount x= 2 of Zn, 3, 5, 6, 7mass%), in order to obtain solder twice [about] the tensile strength of a Sn-Pb eutectic and to obtain high intensity especially at the time of Zn **** 6mass%, the amount of Zn is understood that about 6mass% is good. Moreover, [if scaling of solder used the flux which has a track record as electronic-parts soldering by becoming intense, it becomes impossible to secure wettability, so that there are many amounts of Zn, but] Near amount of Zn 5mass%, since about 85% of wet (rate of a wet flare of a solder ball) of pure Sn is still securable, it is satisfactory. At less than 13mass%, since liquidus temperature is 194 degrees C or more, it becomes difficult to reflow connect Bi at 220 degrees C. In Bi, solidus temperature falls at 150 degrees C or less at more than 16mass%, and the tensile strength in the elevated temperature of a solder ingredient falls. Therefore, margin reservation of the reliability in an elevated temperature becomes difficult. - In order to be able to be equal to a 55-150-degree C temperature cycle accelerated test, even if low as solidus temperature, 160 degrees C or more of 150 degrees C or more are desirably required.

[0028] If it is the solder of such a presentation, soldering of the lead freelancer within a heat-resistant temperature of a glass epoxy board will be attained. The solidus temperature the fusing point of said solder That is, at least 150 degrees C or more, It is desirably considered as 160 degrees C or more (it can be equal to the 150-degree C activity in an elevated temperature). Since the liquidus temperature considers it as 190 degrees C or less (soldering temperature becomes high and, as for making it high, the thermal effect to a substrate and components becomes large) desirably, it realizes a maximum of 195 degrees C or less of substrate mounting with the conventional reflow temperature of 220 degrees C. Moreover, the mounting article using the lead freelancer's solder will be offered also to a heat-resistant low glass epoxy board by such substrate mounting being realizable.

[0029]

[Working example] An example explains this invention still in detail hereafter.

[0030] In the Sn-Zn-Bi3 element-system phase diagram of drawing 1 , only the connection between a rough liquidus temperature and solidus temperature is known. It is a factor with liquidus temperature and solidus temperature important for soldering, and when the yield of bonding is related, the temperature gradient of liquidus temperature and solidus temperature is also an important factor. Then, it decided to investigate thoroughly the solidus temperature and liquidus temperature of the presentation extracted to the fusing point region to need by DSC. Measurement was performed with the heating rate of 2 degrees C/min. [the obtained DSC curve / the configuration in which Susono by the side of the low temperature of an endothermic peak spreads] Since it takes and solidus temperature is not strictly exact by the conventional method (let temperature of the intersection of the tangent drawn towards the elevated-temperature side from the bay before going into an endothermic peak, and the tangent drawn towards the low temperature side from the endothermic peak be solidus temperature), It was considered as the temperature of the point which begins to change the bay of a

DSC curve to a curve by an endothermic peak as a definition.
[0031] Drawing 2 expands the range near pure Sn of drawing 1 , and displays liquidus temperature and solidus temperature. According to this, it goes into the claim range in the range with little Bi to solidus temperature, but since it turned out that it becomes 150 degrees C or less when the amount of Bi(s) became more than 13mass% and it became 160 degrees C or less and more than 16mass%, it is predicted that the temperature gradient of liquidus temperature and solidus temperature becomes large. In this case, since it becomes impossible to take the margin of the reliability in an elevated temperature and becomes easy to produce the problem of a bonding process, as for solidus temperature, it is desirable that it is 160 degrees C or more. Although it turns out in drawing 1 that the Sn-Zn eutectic line of 2 yuan which makes the difference of solidus temperature and liquidus temperature small by liquidus temperature becoming low locally is extended with Sn-9Zn as the starting point to 3 yuan eutectic point Sn-4Zn-56Bi (130 degrees C of fusing points) Since drawing 1 is rough, the exact location of the Sn-Zn eutectic line (curve) of 2 yuan to which the two points are connected does not understand it. Then, in order to know this, it decided to measure minutely about the field shown at the amount 4 of Zn including the field the Sn-Zn eutectic line of 2 yuan is indicated to be on drawing 1 - 6mass% the amount 10 of Bi(s) including the field where solidus temperature becomes 160-170 degrees C - 14mass%. The result was shown in drawing 2 . According to this, the valley where the amount of Bi(s) becomes 10 - 14mass%, and Zn becomes low [liquidus temperature] at 5 - 6mass% of within the limits exists, and it turns out that this is the Sn-Zn eutectic line (drawing 2 heavy line) of 2 yuan. That is, in order to take as small the difference of solidus temperature and liquidus temperature as possible, it turns out that what is necessary is just to choose the presentation on this 2 yuan eutectic line. Since the liquidus temperature of this 2 yuan becomes high rapidly in a presentation field with many amounts of Zn across an eutectic line, it turns out that it is not practical as an object for electronic-parts bonding. However, in order that, as for an eutectic line, Zn of 2 yuan may go into the field beyond 5mass% in the needed field used as the solidus temperature of 150 degrees C or more, 4.5 - 6mass% of the amount of Zn is desirable also in 4 - 6mass% of inside. Next, since liquidus temperature needs to be 195 degrees C or less, it makes the amount of Bi(s) more than 12mass%. Moreover, if solidus temperature is 150 degrees C or more as stated previously, in order to consider less than 16mass% and a margin and to consider it as 160 degrees C or more, less than 13mass% is desirable [the amount of Bi(s)].
[0032] Drawing 3 plots the data which obtained the result of the phase diagram of drawing 2 , and it from the result analyzed still in detail. They are temperature-gradient deltaT of the liquidus temperature at the time of making the amount of Bi(s) 16mass% regularity 14mass% 13mass%, respectively, and solidus temperature, and the connection of the amount of Zn. the amount of Bi(s) -- the time of 13mass% and 14mass% -- Zn5.5mass% -- deltaT is the minimum in order. the time of the amount of Bi(s) being 16mass% -- Zn5mass% -- deltaT is the minimum in order. These results to 4 - 6mass% of Zn is desirable. Even if there are many amounts of Zn, since deltaT increases, it is not desirable from a viewpoint of bonding. [at least] It is not desirable on the problem of the reliability at

the time of bonding to maintain the coexistence region of a liquid and a solid long time at the time of cooling. Next, the liquidus temperature over the amount of Zn is shown. It is desirable from a viewpoint of wettability to lower liquidus temperature as much as possible from a constrain condition with a reflow temperature of a maximum of 220 degrees C. It is made desirable in the viscous viewpoint of wettability and a liquid to carry out a reflow at a temperature high 30-50 degrees C from a fusing point experientially. Therefore, in the case of 220-degree C reflow temperature, a maximum liquidus temperature is 195 degrees C. Drawing 4 is the liquidus temperature over the amount of Zn, when the amount of Bi(s) is considered as 14mass% regularity. whether the amount of Zn increases or it decreases, liquidus temperature rises -- the amount of Zn -- 5mass% -- it becomes the minimum in order. That is, Zn serves as a field which can lower liquidus temperature and can take a small temperature gradient with liquidus temperature and solidus temperature in 4 - 6mass% of the range.

[0033] Next, it wets wet with the amount of Zn, and connection with the rate of a flare (assessment of the wettability over oxidation of Zn) is shown in drawing 5 . Since it wets wet at more than 6mass% and the rate of a flare approaches a steady value, as an amount of Zn from a viewpoint of wettability, less than 6mass% of the amount of Zn is desirable.

[0034] Furthermore, connection resilience was examined. Drawing 6 shows the tensile strength to the amount of Zn, when the amount of Bi(s) is considered as 15mass% regularity. Tensile test conditions are room temperatures and were evaluated at the pull velocity of 0.05 mm/min. Gauge length is 10mm. The specimen was cast by nitrogen-gas-atmosphere mind, and cast was performed with the same cooling rate as reflow conditions. It produced by the electron discharge method so that heat might not be applied to a specimen. the amount of Zn -- 6mass% -- the strong maximum is shown in order, and at more than 6mass%, if the inclination to fall rapidly is shown and the amount of Zn decreases, hardness will fall. Therefore, the range whose amount of Zn is 4 - 6mass% is considered to be a proper range.

[0035] A fusing point (liquidus temperature, solidus temperature) is decided by the combination of the amount of Zn, and the amount of Bi(s). Since wettability etc. is especially influenced greatly about the amount of Zn, various kinds of above-mentioned analyses are needed. As the amount of Bi(s) is shown in drawing 7 , wettability is stable in the range with the large amount of Bi(s). Therefore, the amount of Bi(s) has the large role of the fusing point (liquidus temperature, solidus temperature) adjustment in combination with the amount of Zn.

[0036] The detailed analyses from the field of soldering nature are shown below. The reflow temperature of a maximum of 220 degrees C estimated the wettability of the solder to Cu terminal of a printed plate board. assessment changes a presentation for the rate of a wet flare of a solder ball with a diameter [on Cu board] of 1mm (Sn-5 Zn-xBi (x= 0, 10, 15, 19, 22, 25, 30), Sn-yZn-19Bi (y= 0, 1, 3, 4, 5, 7) measurement was carried out, and the size performed.) The used flux is a rosin system containing 0.2mass% of chlorine. The value of the rate of a wet flare was put on Table 1, and showed drawing 5 and drawing 7 the result as above-mentioned. Wettability is falling, so that there are many amounts of Zn.

[0037]
[Table 1]

【表1】

組成（mass%）	ぬれ拡がり率（%）
Sn	295
Sn-5Zn	240
Sn-9Zn	180
Sn-19Bi	345
Sn-1Zn-19Bi	350
Sn-3Zn-19Bi	296
Sn-4Zn-19Bi	269
Sn-5Zn-19Bi	264
Sn-7Zn-19Bi	260
Sn-5Zn-10Bi	267
Sn-5Zn-15Bi	249
Sn-5Zn-22Bi	252
Sn-5Zn-25Bi	248
Sn-5Zn-30Bi	242

[0038] Moreover, similarly, when the effect of the wettability by the amount of Bi(s) is investigated, by this system, it turns out that it hardly depends for wettability on the amount of Bi(s). Moreover, it turns out that the solder ball near the presentation range of a claim has secured the rate of a wet flare of about 150% of an Sn-9Zn solder ball about 85% of the pure Sn solder ball. Although it depended greatly, and wettability was near the presentation range of a claim and was not more enough for the amount of Zn than this, it turned out that wet required for bonding is obtained. In order to lengthen thinly the soldering paste of presentation within the limits of a claim and to supply it on a substrate by printing on the other hand, Although there are few problems in respect of a wet flare, when an air reflow process is adopted, there is a possibility that solder grains are small in 10 micrometers and the number of diameters, the **** remainder of the grains by scaling of the grains at the time of a reflow may generate it since the solder grain total surface area serves as a big value, and the problem of an electrical property may occur. In order to have solved this problem, it turned out that it is clearable by using N2 reflow or vapor reflow whose soldering is possible, purging O2. Since especially this solder did the firm oxide film when it also exposed the instant to the air, wettability was securable with the device which carries out pasting without exposing to the air. in addition, two kinds, the method which

carries out a reflow of this paste using stronger flux, and is washed, and the method which carries out a reflow using weaker flux, and carries out a reflow by an inert atmosphere and which is not washed, -- having inquired .

[0039] Moreover, the presentation of a sample is changed in order to evaluate in a strong field (Sn-5 Zn-xBi (x= 0, 10, 15, 17, 19, 25) and a Sn-yZn-15Bi (y= 2, 3, 5, 6) room temperature tension test were done, and shown in drawing 6 .). According to it, the tensile strength of Sn-5 Zn-xBi is improving about 50% as compared with the time (two element systems) of x being 0mass%, when x is 10 - 20mass% (three element systems). Since Bi dissolved and this caused solid solution hardening in (Sn) which serves as a matrix in a (Sn)+Zn phase ((Sn) expresses the solid solution of Sn base) at a room temperature by adding Bi and considering it as three element systems, it is considered. Moreover, an elongation percentage decreases to eye others. It seems that weak (Bi) crystallized without the ability dissolving in (Sn) will increase, and tensile strength will be reduced if the amount of Bi(s) is made to increase furthermore. [tensile strength] on the other hand although the tensile strength of Sn-yZn-15Bi serves as the maximum in the y= amount of Zn 5 neighborhood Although this has the thick pure Zn needle crystal of the high intensity in a (Sn)+Zn phase (about 12 kgf(s)/mm2; Japan Institute of Metals metal data book P147), and becomes long with the growth in the amount of Zn and the (Sn) matrix is strengthened The consistency of a needle crystal and a matrix falls as the size of a needle crystal becomes large, and it seems that it is because the effect of a compound consolidation of a needle crystal and a matrix is lost. The value of the tensile strength is shown in Table 2.

[0040]

[Table 2]

【表2】

組成(mass%)	引張強度(kgf/mm^2)
Sn-2Zn-15Bi	5.8
Sn-3Zn-15Bi	8.4
Sn-5Zn-15Bi	9.0
Sn-6Zn-15Bi	9.9
Sn-7Zn-15Bi	8.8

[0041] It turned out that the tensile strength of Sn-(5-6) Zn-(10-20) Bi shows 9 kgf(s)/more than mm2 and eutectic composition twice [about] the value of Sn-Pb according to the two above-mentioned synergistic effects.

[0042] Although this invention targetted the glass epoxy board, it cannot be overemphasized that it can be used for other epoxy system boards and the heat-resistant substrate beyond it, for example, a glass polyimide board, BT (glass fabric base material bismaleido triazine) board, a ceramic substrate,

etc.

[0043] [Example of application to module board mounting] Drawing 8 (a) is an example of power module board mounting at the time of joining the Cu heat sink plate 5 to the ceramic insulated substrates 4, such as Al2O3 which carries the Si chip 3, with Sn-5Zn-13Bi solder 6. Drawing 8 (b) shows Cu heat sink plate which shows the Cu heat sink plate 5 which performed nickel metal plating 7, and the Sn-5Zn-13Bi solder foil 6 rolled to 0.2mm thickness, joins both and is shown in drawing 8 (c) and which carried out preliminary soldering. Generally as for the meta-rise to a ceramic insulated substrate, the architecture of W-nickel-Au8 of nickel metal plating and Au metal plating thin on it is adopted as W conductor. In this case, by connecting the Si chip 3 and the ceramic insulated substrate 4 beforehand with hot Sn-5mass%Sb solder 9 (fusing point: 240 degrees C of liquid phase, 232 degrees C of solid phase) this -- the 220-degree C temperature class bonding using Sn-5Zn-13Bi solder is possible without melting Sn-5mass%Sb solder. As other solder material which connects the Si chip 3 which enables temperature class bonding with Sn-5Zn-13Bi solder, temperature class bonding is possible also for Au-20mass%Sn (fusing point: 280 degrees C of liquid phase) similarly. The AlN board which is excellent in heat leakage nature as an insulated substrate in addition to Al2O3 is used. nickel metal plating (Au metal plating of about 0.2 micrometer or on nickel metal plating) is used on W or Mo meta-rise film as meta-rise material of these ceramic substrates. It is common to cover several micrometers nickel metal plating to Cu plate, and to prevent and use scaling of Cu for it as a rectifier-heat-sink board. The same bonding is possible by performing nickel metal plating similarly to heat sink materials, such as W, Mo, or other compound boards. Moreover, although soldering to Cu plate directly is also possible It is also possible to give 1-2 micrometers of Zn on Cu, in order to maintain the hardness of an alloy layer, and to perform Sn metal plating on it, or to prevent the strength deterioration in an interface on Cu nickel metal plating, by performing Ag metal plating on it further, etc. Since the junction hardness of this solder is high, it is expectable to excel also in the creep resistance in an elevated temperature and heat-resistant fatigue nature. Since Cu heat sink plate can be joined to an insulated substrate in strong flux when the semiconductor etc. is not carried, a zygote with little void is made. Moreover, if temperature class bonding is utilized, it is also possible to make contrary to the above the location which uses solder. Although feed of solder has a common rolling foil, the method which carries out paste printing is possible. The rolling nature of a solder foil is comparatively good, and possible in the range of 0.1-0.2mm thickness. In paste printing, the utilization as reserve solder is main.

[0044] [Example of application to surface mounting] Although it is as having already described above, a soldering paste is used and QFP and chip components are described about the case where it connects with a printed plate board by N2 reflow. Object pitch is 0.5mm pitch and the particle diameter of a solder ball is around 50 micrometers. Cu pad -- pad width; -- it is 0.28mm and Cu foil thickness is 18 micrometers. In order to prevent scaling by Zn, also when making a paste, the creativity which does not expose a solder ball to the air directly was put. Therefore, when it was among the N2 atmosphere with an oxygen density of about 100 ppm or vapor, it turned out that the

underside printed at least wets wet. In respect of wet flare nature, it is less than solder conventionally. However, flux a little stronger against securing sufficient wet was used, and the paste of the washing type which carries out backwashing by water after a reflow was used.

[0045] [Example of application to surface mounting of BGA] Drawing 9 shows the example applied to bonding of the BGA (Ball Grid Array) package which carried out the wire bond of the Si chip 3, and carried out it resin mold 12 by the Au line 11 after pasting the organic group plate 10. The Sn-5Zn-13Bi solder ball 13 of 0.75mm of diameters is made, and it arranges on the terminal of the organic group plate 10, and melts by stronger flux, and a ball 13 is formed on the terminal by the side of the glass epoxy board 14. Terminal pitch is 1.27mm, the diameter of a substrate pad is 0.75mm, the diameter of a package terminal is 0.70mm, and terminal numbers are about 500 pins. The solder bump height after a reflow is about 0.6mm. Irregularity at the head of a ball of 500 pins was a maximum of 20 micrometers. If flux 26 is applied on the glass epoxy board 14, this BGA is carried and N2 reflow is carried out at 220 degrees C, the high yield bonding near 100% will be attained. Since the crevice between BGA and a substrate is large, washing of flux is easy. On the other hand, the washing loess process of flux using low residue flux in consideration of the environmental problem is also possible. Furthermore, the flux loess method depending on reducing [of the volatile solvent with a carboxyl group / slight] is also possible. Bonding on good conditions is possible by carrying out in N2 reflow atmosphere so that it may not oxidize in this case at the time of a reflow, performing about 3 micrometers of nickel metal plating on Cu PATSUDO 15, in order to make it the terminal of a substrate that it is hard to oxidize, and performing 0.1-micrometer Au metal plating on it further. Furthermore, flux loess bonding is more certainly enabled by carrying out surface preparation to scaling of a solder ball, so that the surface may be licked with an excimer laser etc. immediately before. Although the cause of the surface-preparation effect by this excimer laser is unknown, it is said that there is an effect it not only destroys a surface oxide film, but carried out that it is hard to oxidize. In addition, as a method which connects BGA to a glass epoxy board, like QFP mounting, the paste 16 is applied on the Cu pad 15 of a substrate, and the method which carries and carries out a reflow of the BGA on it is also possible. When applying and carrying out a reflow of the paste, reserve solder is turned on the pad side of a substrate. When carrying out a reflow, it connects with solder, such as a little Sn-Bi systems which are excellent in the wettability not only in the same presentation but 220 degrees C, and a Sn-Bi-Ag system, and bonding with the Sn-5Zn-13Bi solder ball by the side of BGA is possible. Even if it fuses from an Sn-5Zn-13Bi solder ball being a principal component, it seldom changes to Sn-5Zn-13Bi solder in a fusing point.

[0046] [Effect of trace element addition] The effect at the time of adding a little Ag, Sb(s), Cu(s), and In(s) to Sn-5Zn-15Bi solder was examined. Ag and Cu are [as opposed to / especially / corrosion] the primary phases of Zn which is not desirable. (close to pure Zn of a component) Since the corrosion of Zn was prevented by making a compound, it turned out that corrosion resistance is improvable. The addition of Ag can improve at 2% or less. The addition of Cu can improve at 1.5% or less. However, it turned out that addition has not influenced refining of Zn directly in Sb and In.

Addition of In is useful for a betterment of wettability, and Sb is useful for the mechanical-strength betterment.

[0047] Drawing 10 draws a line on 30 micrometers of wire diameters in Sn-5Zn-13Bi solder, shows the bonding method which enables bonding of 130-micrometer pitch, and shows the process which carries out a direct wire bond on aluminum conductor of Si chip. (a) is a process which is sticking by pressure the solder which formed the ball by the capillary tube 17 on the aluminum conductor 18 (heat and a supersonic wave may be added). (b) is in the condition which tore off the line in the place clamped and extracted and formed the solder terminal 21 after adhesion. (c) is in the condition which sent out the solder line of fixed length at the head of a capillary tube. If (d) is fused in an arc or laser 19 grade in an inert atmosphere or a reducing atmosphere in an instant, in the head of a solder line, the spherical ball 20 will be formed in an operation of surface tension. Drawing 11 around chip 1 [the solder terminal 21] After performing levelling of a solder bump's height for the formed chip, put the block 22 of a hardened type epoxy resin under a chip in the center beforehand, position a solder bump for the Cu nickel-Au terminal 23 of the organic group plates 14, such as glass epoxy, and heating sticking by pressure is carried out by an inert atmosphere. Flip chip junction is carried out. Since resin does not arrive to a terminal where heating sticking by pressure is carried out, metal junction is possible. If resin 25 is poured after junction and on the perimeter 27 of a chip, in an operation of surface tension, it will be able to knead easily in the crevice between chip perimeter parts, and will cover. the used resin -- 500 to 1000 kgf/mm2 Young's modulus, and coefficient-of-thermal-expansion 15x10~6/degree-C-35x10~6/degree C -- it has physical properties. High reliance mounting is enabled to a glass epoxy board etc. also with a large-sized chip by using this resin. In addition, in order to raise the junction nature of solder and Au for flux loess junction, it is effective to remove the oxide film formed in the solder surface with an excimer laser etc. Although it connected with aluminum conductor of a chip, a spherical solder bump can be made by preparing the meta-rise which wets a terminal area wet in solder by acting as a wetback of what carried out the wire bond in flux. Since this solder has small phase boundary potential with aluminum, there is the advantage by which difference electric corrosion is not generated easily. Furthermore, since there is hardness also in drawing etc. and it is sticky, it does not go out, but it can extend continuously.

[0048]

[Effect of the Invention] [as mentioned above, the Sn-Zn-Bi system solder of this invention] It does not become a cost overrun excluding a harmful element to environment like Pb, but can solder to the glass epoxy board which is stabilized in resource and used from the former with reflow temperature equivalent to conventional Sn-Pb eutectic solder that it can supply with N2 reflow equipment which is the conventional process. This solder has hardness as strong as about (nine to 10 kgf/mm2 tensile strength) 2 times of a Sn-Pb eutectic, and it is excellent in high temperature strength-proof and creep resistance. Compared with the conventional Sn-Pb eutectic solder also as a splice of electronic parts, it has equivalent fatigue resistance.

[0049] Moreover, Pb freelancer's soldering (mounting) to organic insulated substrates, such as a

glass epoxy resin board which was difficult until now, is realized.

[0050] Similarly offer of a mounting article which used and mounted Pb freelancer's solder in organic insulated substrates, such as a glass epoxy resin board, is realized.

[Brief Description of the Drawings]

[Drawing 1] A well-known Sn-Zn-Bi 3 element-system phase diagram (liquidus temperature)

[Drawing 2] The Sn-Zn-Bi3 element-system phase diagram near [which was clarified by the thermal analysis] pure Sn

[Drawing 3] Connection of a temperature gradient with the amount of Zn in a Sn-Zn-Bi system, and liquidus temperature and solidus temperature

[Drawing 4] Connection of the amount of Zn and liquidus temperature in a Sn-Zn-Bi system

[Drawing 5] It wets wet with the amount of Zn in a Sn-Zn-Bi system, and is the connection of the rate of a flare.

[Drawing 6] Connection between the amount of Zn in a Sn-Zn-Bi system, and tensile strength

[Drawing 7] It wets wet with the amount of Bi(s) in a Sn-Zn-Bi system, and is the connection of the rate of a flare.

[Drawing 8] The sectional view of a power module and the process of reserve solder are shown.

[Drawing 9] They are the sectional view of BGA, and the expansion of a terminal area.

[Drawing 10] The cross section which shows the solder bump formation process method is shown.

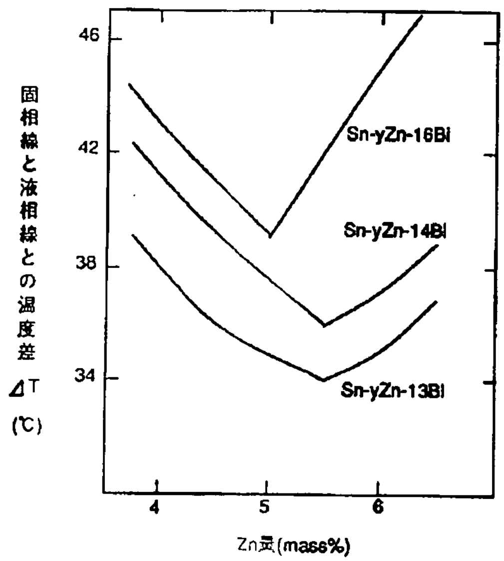
[Drawing 11] The sectional view showing the method of mounting a solder bump method is shown.

[Explanations of letters or numerals]

1. Sn-Zn Eutectic Line of 2 Yuan
2. Sn-Zn-Bi Eutectic Structure Appearance Field of 3 Yuan
3. Si Chip 15.Cu PATSUDO
4. Ceramic Insulated Substrate 16. Paste
5. Cu Heat Sink Plate 17. Capillary Tube
6. Sn-5Zn-13Bi Solder 18.Aluminum Conductor
7. Nickel Metal Plating 19. Arc or Laser
8. W-nickel-Au 20. ball-like ball
9. Sn-5Mass%Sb Solder 21. Solder Terminal
10. Organic Group Plate Block of 22. Epoxy Resin
11. Au Line 23 Cu-nickel-Au Terminal
12. Resin Mold 24. Organic Group Plate
13. Solder ball 25. resin
14. Glass Epoxy Board 26. Flux
27. Chip Perimeter

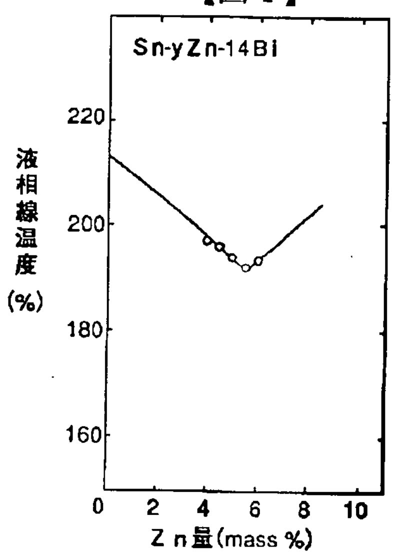
[Drawing 3]

【図3】



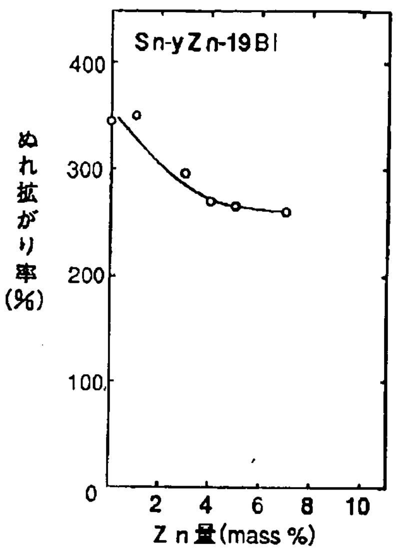
[Drawing 4]

【図4】



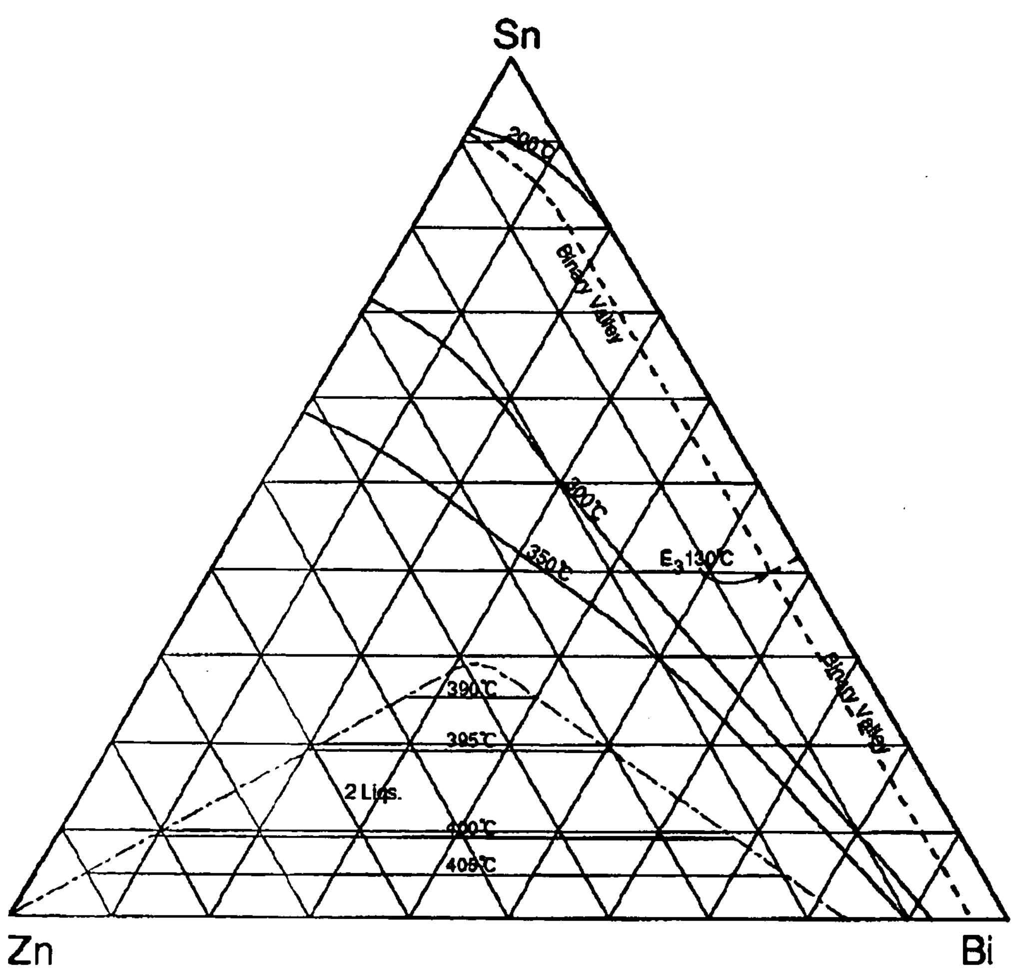
[Drawing 5]

【図5】



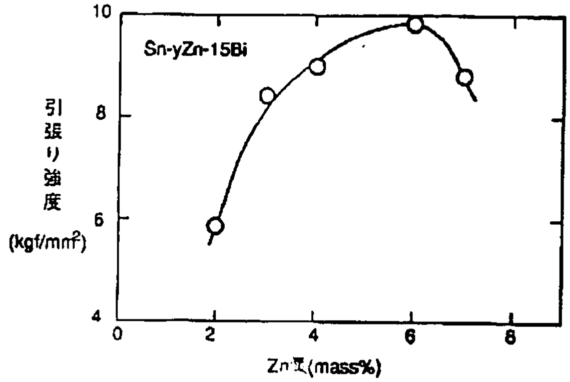
[Drawing 1]

【図1】



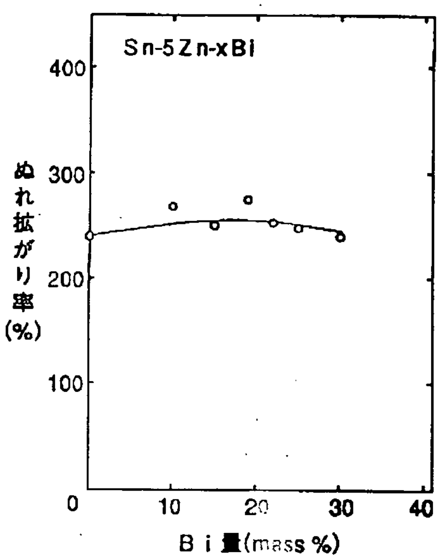
[Drawing 6]

【図6】



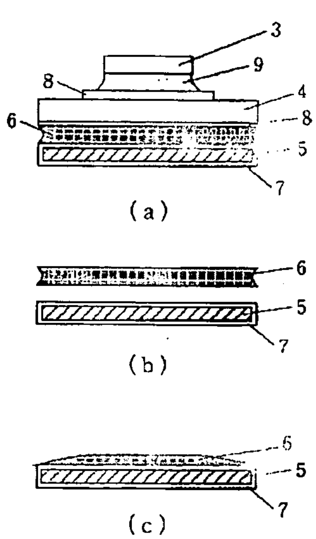
[Drawing 7]

【図7】



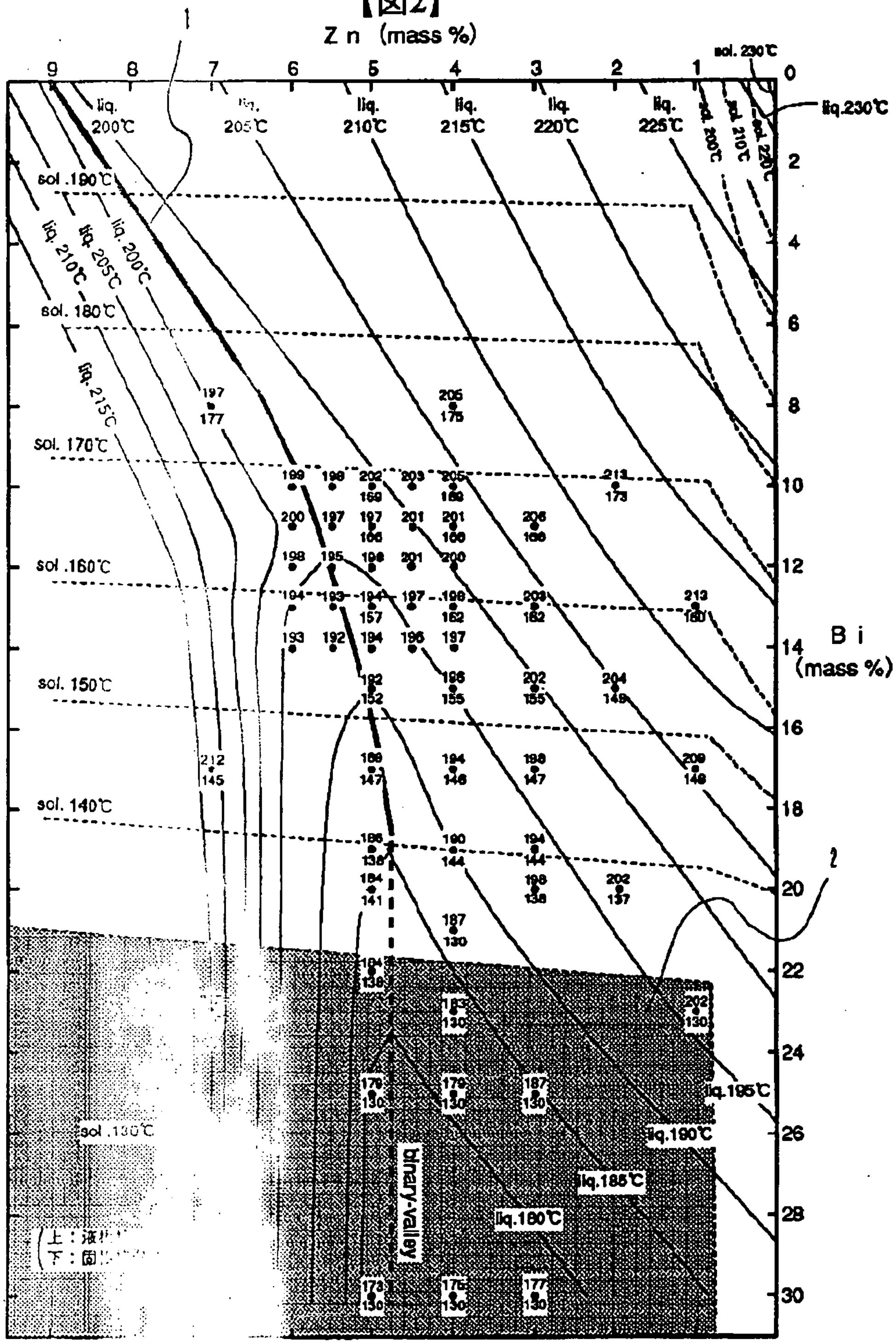
[Drawing 8]

図8



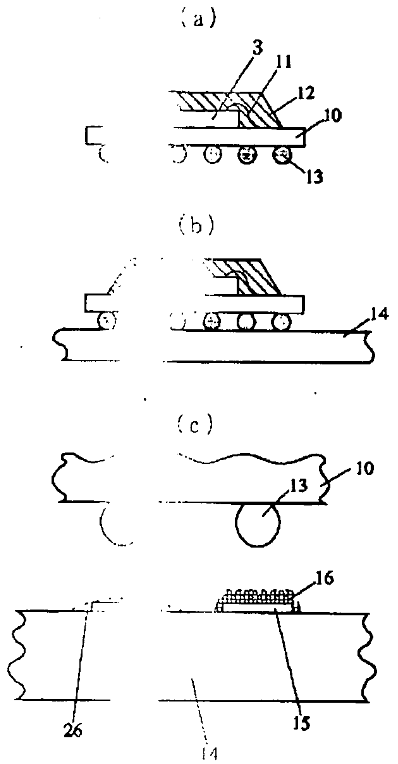
[Drawing 2]

【図2】


Zn (mass %)
Bi (mass %)
liq. 200℃
liq. 205℃
liq. 210℃
liq. 215℃
liq. 220℃
liq. 225℃
liq.230℃
sol. 230℃
sol. 200℃
sol. 210℃
sol. 220℃
sol. 190℃
sol. 180℃
sol. 170℃
sol. 160℃
sol. 150℃
sol. 140℃
sol. 130℃
liq. 195℃
liq.190℃
liq.185℃
liq.180℃
binary-valley
1
2

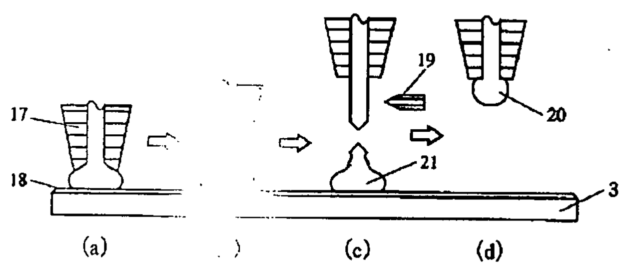
[Drawing 3]

図9



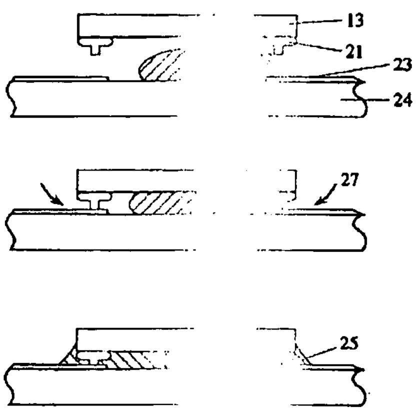
[Drawing 10]

図1 0



[Drawing 11]

図1



[Translation